

Monte Carlo Renormalization Group for Entanglement Percolation

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(Dated: February 1, 2008)

We use a large cell Monte Carlo Renormalization procedure to compute the critical exponents of a system of growing linear polymers. We simulate the growth of non-intersecting chains in large MC cells. Dense regions where chains get in each others' way, give rise to connected clusters under coarse graining. At each time step, the fraction of occupied bonds is determined in both the original and the coarse grained configurations, and averaged over many realizations. Our results for the fractal dimension on three dimensional lattices are consistent with the percolation value.

PACS numbers: 05.10.Cc, 64.60Ak

I. INTRODUCTION

The gelation process in crosslinked polymers has been studied within the context of percolation theory [1, 2, 3, 4], but the rheokinetics [5] of bulk linear polymers as a function of chain length has received less theoretical attention. As the density of chains, and their length increases, the viscosity starts to increase well before the onset of vitrification. [6] It has been proposed [7, 8] that this is due to the entanglement of the polymer chains.

We would like to pose the question of whether the percolation of entanglement clusters is in the same universality class as percolation. We define entanglement clusters starting from ordinary sets of connected bonds. We will consider two such sets connected, as long as they come with a lattice constant of each other, i.e., share the end points of an empty bond. Since the length of the chains, or the average length between entanglements, could introduce a second length scale into the problem, this could potentially lead to a crossover to a different universality class than percolation.

It has been found in two dimensions [9] that the vulcanization process, which involves the crosslinking of long chains, is in the percolation universality class, and that there is a crossover between Self Avoiding Walk and percolation behaviour as a function of the fugacity of the crosslinkers. Similarly, Jan et al. [10] find in three dimensions that the crossover from SAW to percolation exponents already occurs for any finite value of the concentration of initiators (from which the chainlike structures grow), for a mixture of monomers with functionalities ≥ 2 , i.e., again in the presence of crosslinkers. A Monte Carlo simulation in two dimensions reveals [11] that a growth model can cross over from SAW like behaviour to percolation, as a function of the cluster mass.

The percolation of clusters which are not necessarily connected but linked to each other by loops, has also been studied by very large MC computations [12]. These authors find that the new critical point is very close to the ordinary percolation threshold on the cubic lattice, with the eigenvalue of the renormalized occupation probability being indistinguishable from that of the ordinary percolation problem.

In this paper we introduce a special Monte Carlo (MC) Renormalization Group procedure to investigate the universality class for the entanglement phase transition of a linear polymer system, in three dimensions and with no crosslinkers (or monomers with functionality greater than 2) present. The polymerization process is modeled by growing non-intersecting chains from a set of randomly chosen sites on a cubic lattice. Chains which occupy nearest neighbor sites on the lattice are considered to be part of the same connected cluster, and coarse grain to occupied bonds.

In the next section, we present the simulations and the MC renormalization group procedure. In section 3 we present an analysis of the results. We conclude with a discussion in section 4.

II. MC SIMULATIONS AND THE RENORMALIZATION GROUP

In this section we describe a Monte Carlo renormalization group procedure, to deal with the percolation of entangled clusters of linear polymers. Since the long linear chains of the growing bulk polymer cannot be accommodated in small cells, we start by simulating the polymer growth on relatively large lattices. However we make a different choice than the one made by Swendsen [13, 14, 15] in the way that the MC renormalization group is introduced, as illustrated schematically in Fig.1.

The MC Renormalization Group procedure which we use consists of paving the large MC cell by small cells on which one performs a coarse graining transformation. [16] This induces an RG transformation on the bond occupation probability, averaged over many independent realizations.

In the conventional MC renormalization group procedure, the coarse graining is done in one step [13, 14, 15]. In the case of percolation, this would mean coarse graining the large MC cell to one occupied or empty bond - i.e., one asks the question whether the cell is spanned by a connected cluster or not. Adopting the conventional definition of a connected cluster, this one-step coarse graining procedure is clearly not appropriate in our case,

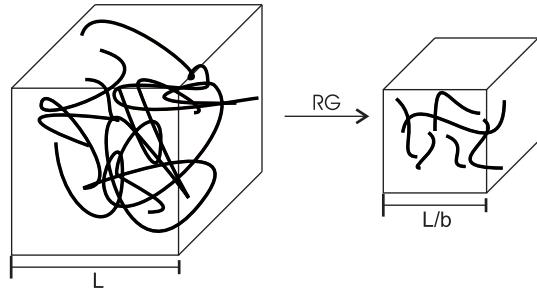


FIG. 1: We use a set of kinetic growth rules, to grow a mass of non-intersecting linear chains in 3 dimensions. Then we apply an RG transformation to get the new coarse-grained system.

since for non-intersecting linear chains, the MC cell will be spanned in case there is at least one chain that grows across it, and otherwise not. This does not describe the physical problem at hand.

The effect which we are trying to model has to do with linear chains that do not intersect, but nevertheless get physically close to each other in dense regions where they constrain each others' motion, at least on short time scales, and thus form an effective three-dimensional network. We look, therefore, for a way in which we can capture this effectively three dimensional behaviour, and the answer lies in making a coarse graining with a scale factor b smaller than the linear size L of the large cell. We will illustrate below, that chains which are non intersecting can, under coarse graining, go to branched structures, which behave very much like ordinary percolation clusters.

A. The Kinetic Growth Model for Linear Polymers

We have generated our configurations on a cubic lattice with linear dimension L and periodic boundary conditions. We start from an empty lattice, and then place C initiators at randomly chosen lattice sites. As the chains grow, the initiators are displaced in the growth direction and mark the “active end” of the chains. We don't allow a chain to intersect itself or the other chains during this process. If the chain hits a dead end, it stops growing.

The growth rules are as follows. During one time step, from time t to $t + 1$, we consider each chain one by one, look at the active end of the chain and count the number of empty nearest neighbor sites. If this number is zero, the chain is trapped, and we proceed to the next chain. If the number is greater than zero, with *growth probability* k we extend the chain to one of these empty sites, chosen at random. (This extra parameter k gives us the possibility of probing arbitrarily small increments in the occupation probability on our finite cell.) We mark this new location as the active end of the chain, and place a bond between the old and the new location of this active end. After

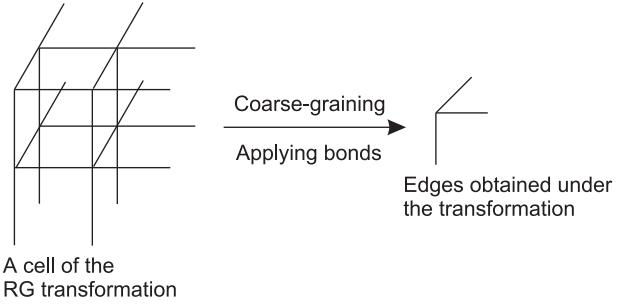


FIG. 2: One cell of the RG transformation. Under our coarse-graining rule one cell goes to at most three bonds in the three Cartesian directions.

this process has been applied to all the chains, one gets the configuration at time $t + 1$.

We use this set of kinetic growth rules, to grow a mass of non-intersecting linear chains in relatively large cells, consisting of cubic lattices of linear size $L = 8, 16, 32$.

B. Compactification and Coarse-Graining

In Fig. 2, we display the small cells with which our lattice will be paved, in order to perform the coarse graining transformation. This choice for the coarse graining rule has been used by Reynolds et al. [17] and Bernasconi [18]. Under our coarse-graining rule each cell (with $3b^3$ bonds, where b is the rescaling factor, here chosen to be 2) goes to at most three bonds in the coarse-grained lattice.

Before we coarse grain, we perform a compactification of our randomly connected clusters by connecting nearest neighbor occupied sites, which are not already connected by a bond. (See Fig. 3) This is motivated by the fact that in dense regions, chains which physically get in each others' way are not chemically connected, but nevertheless contribute to the instantaneous shear modulus of the effective network.

We determine the state of the bonds in the coarse-grained lattice by considering the configurations in each small cell, as illustrated in Fig. 4. We look for a path which spans the cell in each Cartesian direction. If there is at least one such path this cell goes to an occupied bond in this direction in the coarse-grained lattice. Otherwise, it goes to an empty bond. By applying this rule to each small cell in the original lattice we get the new coarse-grained lattice.

It can be noticed in Fig. 4 that the occupied bonds spanning the small cell in the horizontal and the vertical directions are not chemically connected, and yet, (even without the bonds added for compactification) they go, under coarse graining to an occupied junction.

We now compute the fraction of occupied bonds in both the original and coarse-grained lattices, $p(t)$ and $p'(t)$, where we also count the bonds added in the compactification process. These are averaged over many in-

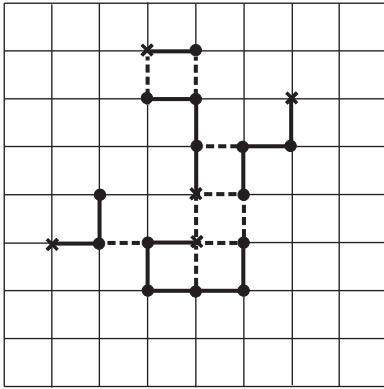


FIG. 3: An illustration of our linear polymer system in 2 dimensions at time t . Solid lines show the occupied bonds, solid dots indicate the monomers. Cross marks show the active ends of the chains, from which a chain grows. The dashed lines show the bonds added in the compactification procedure; these are included in the computation of $p(t)$.

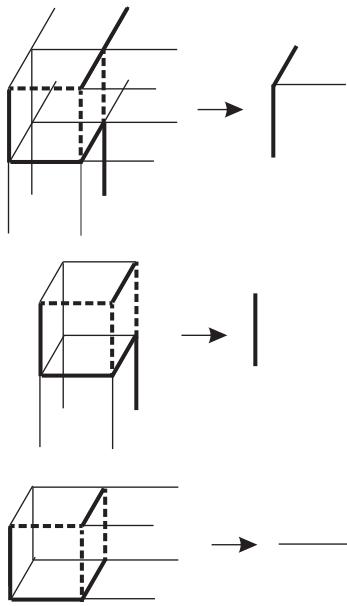


FIG. 4: An example of our coarse-graining rule. In each Cartesian direction, we look for a path which spans the cell in this direction. See text.

dependent runs, to find $\langle p(t) \rangle$ and $\langle p'(t) \rangle$, for each time t . Eliminating t , the coarse graining procedure leads to a renormalization group transformation on the average occupation probability, as shown in Figure 5. The fixed point of the RG transformation and the RG eigenvalue are computed from the MC data, leading to the value of the critical exponent we are interested in.

III. FINITE SIZE SCALING AND THE FRACTAL DIMENSION

The correlation length,

$$\xi \sim (p - p^*)^{-\nu} , \quad (1)$$

for p very close to the critical point p^* (the fixed point of the RG transformation) exceeds L . From then on, $\xi \sim L$, i.e., it behaves like a constant with respect to $(p - p^*)$. In other words, the relationship in Eq.(1) breaks down and a finite size scaling analysis is in order. [1]

The mass contained in the incipient infinite cluster, $\Delta M \sim L^{D_f}$, where D_f is the fractal dimension of the percolation cluster, so that $P_\infty = \Delta M/V \sim L^{-\beta/\nu} \sim L^{D_f-d}$. We may also show that the mass M_0 contained in the rest of the finite clusters scales like $M_0/V \sim L^{(2-\tau)D_f}$, with $(2-\tau)D_f = D_f - d$. Thus, the total concentration $p = (\Delta M + M_0)/V \equiv M/V$ of occupied bonds scales like

$$p \sim L^{D_f-d} . \quad (2)$$

We will make use of this fact to compute the fractal dimension of the percolation cluster, which can be directly related to the other known critical exponents, e.g. via $D_f = (\beta + \gamma)/\nu$. [4]

From (2), we see that under a rescaling transformation $L \rightarrow L' = L/b$, $M \rightarrow M' \sim b^{-D_f} M$, so that

$$p' = \frac{M'}{V'} \sim b^{d-D_f} p . \quad (3)$$

At the fixed point of the RG transformation, p^* , with $\lambda \equiv dp'/dp|_{p^*}$, one has, $\lambda = b^{d-D_f}$, or

$$D_f = d - \frac{\ln \lambda}{\ln b} . \quad (4)$$

In Fig. 5, we plot $\langle p'(t) \rangle$ versus $\langle p(t) \rangle$ for $L=32$ where the averages have been performed over 10^4 independent runs, with $C = 0.02 \times L^3$ and $k = 0.01$. Notice that $p^* \approx 0.02$ is much smaller than the expected value for percolation on a cubic lattice (0.2488) [1]. We have varied C between 1 to 9% of the lattice points, and a fixed point p^* has been found for all these different C values, although the value of p^* decreases with decreasing C . This can be seen to result from an effective length scale introduced by the increasingly long chains growing from fewer and fewer initiators, i.e., an effective lattice spacing of the order of $C^{-1/3}/L$ [10].

We obtain λ by making a linear fit to the data around this point, and we obtain the value of the critical exponent D_f from Eq. (4). Our results are given in Table 1. Within our error bars we have not found any dependence of the RG eigenvalue on the concentration of initiators, within the range of values we have considered. The errors reported in Table 1 are those arising from taking one standard deviation of each of our data points reported in the inset of Fig. 5. The best value of D_f for percolation clusters in three dimensions, obtained from simulation

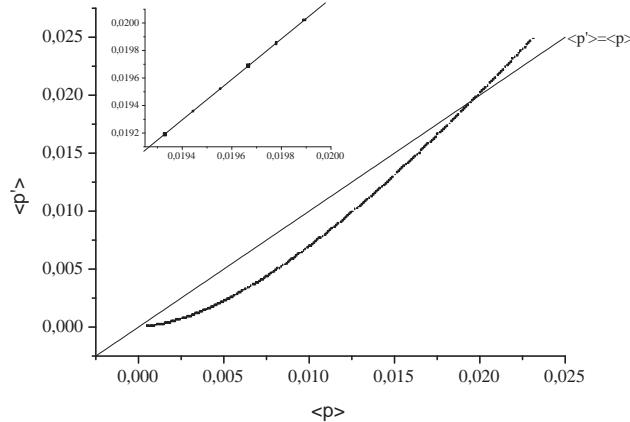


FIG. 5: A plot of $\langle p' \rangle$ v.s. $\langle p \rangle$ for the 2% concentration of initiators on an $L = 32$ lattice. The data points are averaged over 10^4 independent runs. The inset shows the same graph in the vicinity of the fixed point p^* .

TABLE I: λ and D_f values obtained by our simulations.

L	8	16	32
λ	1.476	1.479	1.472
D_f	2.438	2.436	2.442
ΔD_f	0.004	0.002	0.001

results [19] is 2.53 ± 0.03 . Given that we are performing a finite cell real space renormalization group calculation, our results are consistent with the percolation fractal dimension.

IV. DISCUSSION

The physics of bulk linear polymers is an extremely interesting and rapidly growing field. As the average

molecular weight (or chain length) grows, bulk linear polymers are known to exhibit many of the properties of ordinary gels, such as resistance to shear and the capacity to take up solvent and swell, while retaining their original shape. [20] This behaviour is present even in linear polymers like PMMA (Poly-methyl methacrylate) where inter-chain interactions [21, 22] are extremely weak, and therefore must arise from purely geometrical effects, in other words entanglements. [23, 24] In this context we use “entanglement” to mean a dense region where chains physically impede the motion of other chains, and not in the mathematically precise sense of knots [12, 25, 26, 27].

The transition to a regime where the presence of an entanglement network can be ascertained via dilatometric techniques [28] takes place before or around the onset of the “gel effect,” namely the characteristic rapid growth in the rate of polymerization [29, 30]. This effect arises due to the transition to a diffusion-limited regime, where end to end termination of chains is essentially suppressed, so that single chains grow rapidly [23, 28, 29, 30]. Its onset has been conjectured to be due to the entanglement of the linear chains [7, 8].

Defining entanglement clusters as chains which will be considered connected if they happen to pass through nearest neighbor sites, we set out to study the scaling behaviour in the vicinity of the entanglement percolation threshold in three dimensions. We have demonstrated, via a modified MC Renormalization Group, that for realistic concentrations of initiators, entangled clusters of linear chains have the same fractal dimension as ordinary percolation, although the entanglement percolation threshold is much lower than for standard bond percolation on a cubic lattice.

Acknowledgements

We would like to thank Nihat Berker for useful comments. One of us would like to acknowledge partial support from the Turkish Academy of Sciences.

[1] D. Stauffer and A. Aharony, *Introduction to Percolation Theory*, (Taylor and Francis, London, 1992).
[2] D. Stauffer, A. Coniglio, and M. Adam, *Adv. Polym. Sci.* **44**, 103 (1982).
[3] H.J. Herrmann, D.P. Landau, D. Stauffer, *Phys. Rev. Lett.* **49**, 412 (1982).
[4] H.J. Herrmann, *Phys. Rep.* **136**, 153 (1986).
[5] D.S. Achilias and C. Kiparissides, *Macromolecules*, **25** 3739 (1992); M. Cioffi, A.C. Hoffmann, L.P.B.M. Janssen, *Nonlin. Analysis* **47**, 897 (2001); L. Gu, S. Zhu, A.N. Hrymak and R.H. Pelon, *Polymer* **42**, 3077 (2001); see J.G. Qin, W.P. Guo and Z. Zhang, *Polymer* **43**, 1163 (2002) for more references.
[6] M.T. Cicerone, P.A. Wagner, and M.D. Ediger, *J. Phys. Chem B* **101**, 8727 (1997).
[7] P.-G. de Gennes, *Scaling Concepts in Polymer Physics*, (Cornell University Press, Ithaca, 1988), pp.54.
[8] M. Doi and S.F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986).
[9] A. Coniglio and M. Daoud, *J. Phys. A: Math. Gen.* **12**, L259 (1979).
[10] N. Jan, A. Coniglio, H.J. Herrmann, D.P. Landau, F. Leyvraz, and H.E. Stanley, *J. Phys. A* **19**, L399 (1986).
[11] A. Ordemann, H.E. Roman, A. Bunde, *Physica A* **266**, 92 (1999).
[12] Y. Kantor and G.N. Hassold, *Phys. Rev. Lett.* **60**, 1457 (1988).
[13] R. H. Swendsen, *Phys. Rev. Lett.* **47**, 1159 (1981).

- [14] R. H. Swendsen, in T. W. Burkhard and J. M. J. van Leeuwen eds., *Real Space Renormalization* (Springer Verlag, Heidelberg, 1982).
- [15] R. H. Swendsen, “Monte Carlo Renormalization Group”, in M. Levy, J-C Le Guillou, and J. Zinn-Justin eds., *Phase Transitions: Cargese 1980* (Plenum, NY 1982), p.395.
- [16] P. J. Reynolds, H. E. Stanley, and W. Klein, Phys. Rev. B **21**, 1223 (1980).
- [17] P. J. Reynolds, H. E. Stanley, and W. Klein, J. Phys. C **10**, L167 (1977).
- [18] J. Bernasconi, Phys. Rev. B **18**, 2185 (1978).
- [19] H.J. Herrmann, H.E. Stanley, Phys. Rev. Lett. **53** 1121, (1984).
- [20] Y. Yilmaz, A. Erzan, and Ö. Pekcan, “Slow regions percolate near glass transition,” cond-mat/0207202.
- [21] A. Saiani, J. Spevacek, and J.M. Guenet, Macromolecules **31**, 703 (1998).
- [22] I. Erukhimovich, M.V. Thamm, and A.E. Ermoshkin, Macromolecules **34**, 5653 (2001).
- [23] S. Zhu, Y. Tian, A.E.Hamielec, and D.R. Eaton, Polymer **31**, 154 (1990).
- [24] Y. Tian, S. Zhu, A.E. Hamielec, D.B. Fulton, and D.R. Eaton, Polymer **33**, 384 (1992).
- [25] A.E. Holroyd, Math. Proc. Cambridge Phil. Soc. **129**, 231 (2000).
- [26] A.E. Holroyd, “Entanglement and rigidity in percolation models,” preprint, www.math.ucla.edu/~holroyd/research.html.
- [27] G.R. Grimmet and A.E. Holroyd, Proc. London Math. Soc.(3)**81**, 485 (2000).
- [28] O. Okay, D. Kaya, Ö. Pekcan, Polymer **40**, 6179 (1999).
- [29] O. Okay, Polymer **35**, 796 (1994).
- [30] O. Okay, Polymer **35**, 2613 (1994).